# Statistical and Thermal Physics: Homework 17

Due: 1 May 2020

## 1 Partition functions for artificial systems

Consider three systems, each with a single particle at temperature  $10^5$  K. System A has two states, one with energy  $0\,\mathrm{eV}$  and the other with  $10\,\mathrm{eV}$ . System B has three states, one with energy  $0\,\mathrm{eV}$  and the other two each with  $10\,\mathrm{eV}$ . System C has four states, two each with energy  $0\,\mathrm{eV}$  and the other two each with  $10\,\mathrm{eV}$ . Let  $Z_A$  be the partition function for system A, etc,....

- a) Which of the following is true? Explain your answer.
  - i)  $Z_A = Z_B = Z_C$ .
  - ii)  $Z_A = Z_B \neq Z_C$ .
  - iii)  $Z_A = Z_C \neq Z_B$ .
  - iv)  $Z_B = Z_C \neq Z_A$ .
  - v) None of the partition functions are the same.

Now suppose that system A has a single particle and two states, one with energy 0 eV and the other with 10 eV. System B has two distinguishable particles and each could be in one of the two states of system A.

b) Is  $Z_A = Z_B$  in this case? Explain your answer.

### 2 Interstellar heat bath

The molecule CN is often found in interstellar molecular clouds. This molecule has many states associated with rotational motion. Observations indicate that about 10% of all such molecules are in any single one of the first three excited states, each of which has the same energy,  $4.7 \times 10^{-4} \, \mathrm{eV}$ , above the ground state. The remaining 70% of the molecules are in the ground state. Assuming that the molecules are in thermal equilibrium with a heat bath, determine the temperature of the heat bath.

This addresses a famous issue in cosmology and is discussed in detail in P. Thaddeus, *Annual Review of Astronomy and Astrophysics*, vol. 10, p. 305 (1972).

## 3 Two level system

Consider a system consisting of a single particle that could be in one of two possible states. The energies of the states are  $-\epsilon$  and  $\epsilon$ .

- a) Determine an expression for the partition function of the system.
- b) Determine an expression for the mean energy of the system.

- c) Determine an expression for the heat capacity of the system.
- d) Suppose that the energies of each state are each changed by adding the same constant energy,  $E_0$ . Show that this will change the partition function and the mean energy of the system according to  $\overline{E} \to \overline{E} + E_0$ . Show that it will not change the probabilities with which the system will be in either state.

#### 4 One-dimensional harmonic oscillators: canonical ensemble

Consider an ensemble of N identical distinguishable quantum harmonic oscillators. The states of a single oscillator are labeled by  $n = 0, 1, 2, \ldots$  and these have energy

$$E = \hbar\omega \left( n + \frac{1}{2} \right).$$

These are all in equilibrium with a bath at temperature T.

a) Use the canonical ensemble formalism (partition function, etc., ...) to show that the mean energy for the ensemble is

$$\overline{E} = N\hbar\omega \left(\frac{1}{2} + \frac{e^{-\hbar\omega\beta}}{1 - e^{-\hbar\omega\beta}}\right) = N\hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega\beta} - 1}\right)$$

- b) Determine the specific heat capacity (heat capacity per particle) of the ensemble.
- c) Determine the mean energy and heat capacity in the high temperature limit  $kT \gg \hbar\omega$ .
- d) Show that the mean energy in the low temperature limit  $(kT \ll \hbar\omega)$  is

$$\overline{E} = N\hbar\omega \left(\frac{1}{2} + e^{-\hbar\omega/kT}\right).$$

e) Determine the specific heat capacity in the low temperature limit and verify that  $C \to 0$  as  $T \to 0$ . This behavior of the heat capacity is also required in all cases by the third law of thermodynamics.

## 5 Third law of thermodynamics

Suppose that a system has states, labeled s = 1, 2, 3, ..., and that these all have distinct energies that satisfy  $E_1 < E_2 < E_3 < ...$  We would like to consider whether it is possible that the lowest energy state is occupied with certainty and none of the other states are occupied with certainty. To do this we require that the probabilities satisfy

$$\frac{p_2}{p_1} = \frac{p_3}{p_1} = \frac{p_4}{p_1} = \dots = 0. \tag{1}$$

- a) Suppose that Eq. (1) is true. Find the temperature of the system.
- b) Show that if  $T \to 0$  then Eq. (1) is true.
- c) Determine the entropy of the system as  $T \to 0$ .

The result  $\lim_{T\to 0} S = \text{(correct answer to part c))}$  is the third law of thermodynamics. The consequences of this for heat capacities is discussed in section 2.20 of the text.

d) Consider the thermal expansion coefficient at constant pressure of any system

$$\left(\frac{\partial V}{\partial T}\right)_P$$

Use one of the Maxwell relations to relate this to a derivative of entropy and then use the third law to show that the thermal expansion coefficient must approach zero as  $T \to 0$ .

# 6 Semi-classical gas

The semi-classical "particle in a box" model of a gas of distinguishable particles results in the Helmholtz free energy

$$F = -NkT \left[ \ln V + \frac{3}{2} \ln \left( \frac{mkT}{2\pi\hbar^2} \right) \right]$$

where m is the mass of a gas molecule.

- a) Determine the entropy of this gas.
- b) Determine the chemical potential of this gas.
- c) Consider two ideal gases that are initially isolated. Gas A consists of molecules with a smaller mass, gas B of molecules with a larger mass. Initially each has the same volume, number of particles and temperature. The two gases are allowed to interact and can exchange particles and energy. In which direction will particles flow as the gases reach equilibrium? Explain your answer.

## 7 Mean values of position and momentum for a particle in one dimension

Consider a particle that can move in one dimension. Let x and p denote the position and momentum of the particle respectively. Suppose that the energy of the particle is

$$E = \frac{p^2}{2m} + U(x)$$

where U(x) is any potential energy.

a) Show that the partition function takes the form

$$Z = Z_x Z_p$$

where

$$Z_x := \alpha_x \int e^{-U(x)\beta} \mathrm{d}x$$

and

$$Z_p := \alpha_p \int e^{-p^2 \beta/2m} \mathrm{d}p$$

where  $\alpha_x$  and  $\alpha_p$  are constants that are independent of temperature.

The constants  $\alpha_x$  and  $\alpha_p$  are irrelevant for the thermodynamics that follows and can both be set equal to 1.

b) The probability density for the position of the particle, regardless of its momentum is

$$p(x) = \frac{1}{Z} \int e^{-E\beta} dp.$$

Show that

$$p(x) = \frac{1}{Z_r} e^{-U(x)\beta}.$$

c) The mean value of the position, regardless of momentum, is

$$\overline{x} := \int x \, p(x) \mathrm{d}x.$$

Show that

$$\overline{x} = \frac{1}{Z_x} \int x e^{-U(x)\beta} dx.$$

- d) Evaluate  $\overline{x}$  for a one dimensional classical harmonic oscillator.
- e) Consider a particle that is trapped in a vertical region  $0 < y \le \infty$  and which is subject to potential u(y) = mgy where m > 0. Sketch the potential and indicate its minimum. If a particle were released from rest at any y > 0, where would you expect to eventually find it? Now suppose that the particle is in contact with a heat bath at temperature T. Determine an expression for  $\overline{y}$ . How does this compare to your previous expectation? Comment on this as  $T \to 0$  and  $T \to \infty$ .

$$Z_{c} = e^{-C\beta} + e^{-C\beta} + e^{-1C\beta} + e^{-1C\beta}$$

$$= 2 + 2e^{-1C\beta}.$$

So 
$$Z_B > Z_A$$
  
 $Z_C > Z_A$ 

ZB= 1+e10B+e-1CB+e-20B

Icel

$$= ZA^2$$

About 10% are in each of the three excited states =0 70% " grand state.

The fraction in each state is  $f_s = P_s = e^{-E_s B}/Z$ 

Then fraction in ground state is  $f_0 = 0.7$ " one excited " is  $f_1 = 0.1$ 

So  $\frac{f_1}{f_0} = \frac{e^{-E_1\beta/2}}{e^{-E_0\beta/2}} = e^{-(E_1-E_0)\beta}$ 

 $\exists D \quad \ln\left[\frac{f_1}{f_0}\right] = -\left(E_1 - E_0\right)\beta = -\left(E_1 - E_0\right)/k7 \quad \exists D \quad T = \frac{\Delta E}{k \ln\left(\frac{f_1}{f_0}\right)}$ 

 $T = \frac{-4.7 \times 10^{-4} \text{ eV}}{8.61 \times 10^{-5} \text{ eV/k} \ln \left(\frac{0.1}{0.7}\right)}$ 

=0 T= 2.8 K

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a) 
$$Z = \sum e^{-E_3 \beta}$$
  
 $= e^{-(-\epsilon)\beta} + e^{-\epsilon \beta} = e^{-\epsilon \beta} + e^{-\epsilon \beta}$   
 $= 2 \cosh(\epsilon \beta)$ 

b) 
$$\overline{E} = -\frac{\partial}{\partial \beta} \ln Z$$

$$= -\frac{1}{7} \frac{\partial}{\partial \beta} \left\{ e^{\xi \beta} + e^{-\xi \beta} \right\} = -\left( \varepsilon e^{\xi \beta} - \varepsilon e^{-\xi \beta} \right) / \left( e^{\xi \beta} + e^{-\xi \beta} \right)$$

$$= -\varepsilon \left\{ e^{\xi \beta} - e^{-\xi \beta} \right\} / \left( e^{\xi \beta} + e^{-\xi \beta} \right)$$

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$$= -\varepsilon \left\{ e^{\xi \beta} - e^{-\xi \beta} \right\} / \left( e^{\xi \beta} + e^{-\xi \beta} \right)$$

$$= 0 \quad \overline{E} = -\frac{\epsilon \left[ e^{+\epsilon B} - e^{-\epsilon B} \right]}{e^{\epsilon B} + e^{-\epsilon B}} = -\epsilon \quad \frac{\sinh \epsilon B}{\cosh \epsilon B}$$

C) 
$$C = \frac{\partial \overline{E}}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial \overline{E}}{\partial B}$$
 and  $B = \frac{1}{kT}$   
But  $\frac{\partial \beta}{\partial T} = -\frac{1}{kT^2} = 0$   $C = -\frac{1}{kT^2} \frac{\partial \overline{E}}{\partial B}$ 

Now 
$$\frac{\partial \vec{E}}{\partial \beta} = \frac{\partial}{\partial \beta} \left[ \frac{\sinh \epsilon \beta}{\cosh \epsilon \beta} \right] = \frac{\epsilon^2 \cosh \epsilon \beta \cosh \epsilon \beta}{\cosh^2 \epsilon \beta} = \frac{\epsilon^2 \cosh \epsilon \beta \cosh \epsilon \beta}{\cosh^2 \epsilon \beta}$$

$$= \frac{e^{2} \left[ \cosh^{2} \epsilon B - \sinh^{2} \epsilon B \right]}{\cosh^{2} \epsilon B}$$

But 
$$\cosh^2 x - \sinh^2 x = \frac{(e^x + e^{-x})^2 - (e^x - e^{-x})^2}{4}$$
  
= 1

$$\frac{\partial \overline{E}}{\partial B} = -\frac{E^2}{\cosh^2 \epsilon B}$$

$$= \sqrt{C} = \pm \frac{\epsilon^2}{kT^2} \frac{1}{\cosh^2 \epsilon_B} = \frac{\epsilon^2}{kT^2} \frac{4}{\left[e^{\pm \epsilon_B} + e^{-\epsilon_B}\right]^2}$$

d) Here 
$$Z = e^{-(\epsilon + E_0)B} + e^{-(\epsilon + E_0)B}$$
  
=  $e^{-\epsilon B} e^{-\epsilon B} + e^{-\epsilon B} e^{-\epsilon B}$ .

Then 
$$\overline{E}_{new} = -\frac{\partial}{\partial B} \ln 2new = -\frac{\partial}{\partial B} \ln \left[ e^{-E_0B} \frac{1}{2} dd \right]$$

$$= -\frac{\partial}{\partial B} \left[ -E_0B + \ln 2 dd \right]$$

$$= E_0 + E_0 dd$$

$$= E_0 + E_0 dd$$

a) 
$$Z = (Z_{single})^N$$

The single oscillator states we labeled 
$$n=0,1,2,3,...$$
 and have energy  $E_n=\hbar\omega(n+\frac{1}{2})$ . So

$$Z = \sum_{n=0}^{\infty} e^{-E_n\beta} = \sum_{n=0}^{\infty} e^{-\hbar\omega(n+\frac{1}{2})\beta}$$

$$= e^{-\hbar\omega\beta/2} \sum_{n=0}^{\infty} e^{-\hbar\omega\beta n}$$
geometric series  $r = e^{-\hbar\omega\beta}$ 

$$= e^{-\hbar\omega\beta/2} \frac{1}{1-e^{-\hbar\omega\beta}}$$
 since  $e^{-\hbar\omega\beta} < 1$ 

Thus

$$Z = e^{-\hbar\omega\beta N/z} \left(\frac{1}{1-e^{-\hbar\omega\beta}}\right)^N$$

Now

$$= -\frac{2}{5\pi} \left\{ \ln \left[ e^{-\hbar \omega \beta N/2} \left( \frac{1}{1 - e^{-\hbar \omega \beta}} \right)^{N} \right] \right\}$$

$$\frac{1}{2} + \frac{1}{1-e^{-h\omega\beta}}$$

$$= \frac{1}{2} \left\{ 1 + 2 \frac{e^{-h\omega\beta}}{1-e^{-h\omega\beta}} \right\} = \frac{1}{1-e^{-h\omega\beta}}$$

$$= \frac{1}{2} \left\{ 1 + 2 \frac{e^{-h\omega\beta}}{1-e^{-h\omega\beta}} \right\} = \frac{1}{1-e^{-h\omega\beta}}$$

$$\overline{E} = \underbrace{\frac{N \hbar \omega}{Z}}_{\frac{1}{2}} \underbrace{\frac{1+e^{-\hbar \omega B}}{1-e^{-\hbar \omega B}}}_{\frac{1}{2}} = D \left( \overline{E} = \frac{N \hbar \omega}{Z} \left( \frac{e^{\hbar \omega \beta_{+} 1}}{e^{\hbar \omega \beta_{-} 1}} \right) \right)$$

b) 
$$C = \frac{\partial \overline{E}}{\partial t} = \frac{N \hbar \omega}{Z} \frac{\partial}{\partial T} \left[ \frac{1}{Z} + \frac{1}{e^{\frac{1}{\hbar \omega}} B_{-1}} \right]$$

and 
$$\frac{\partial}{\partial T} = \frac{\partial}{\partial B} \frac{\partial B}{\partial T}$$

$$\beta = \frac{1}{kT} = 0$$
  $\frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}$ 

$$= \frac{N \hbar \omega \left(-\frac{1}{kT^2}\right) \frac{\partial}{\partial \beta} \left[\frac{1}{e \hbar \omega \beta - 1}\right]}{2 k T^2}$$

$$= + \frac{N \hbar \omega}{2 k T^2} \frac{e \hbar \omega \beta}{\left(e \hbar \omega \beta - 1\right)^2}$$

$$C = Nk \left(\frac{\hbar w}{kT}\right)^2 \left(\frac{e^{\hbar w\beta}}{e^{\hbar w\beta}-1}\right)^2$$

SO 
$$E \approx \frac{N \frac{1}{2} \left( \frac{2 + h w \beta}{k \mu \beta} \right)}{2}$$

$$\approx \frac{N}{2} kT (2+\hbar wB) \approx NkT$$

Then 
$$C \approx Nk \left(\frac{\hbar \omega}{kT}\right)^2 \frac{1}{\left(1+\hbar \omega B - 1\right)^2} \approx C \approx Nk$$

$$\overline{E} = \frac{N\hbar\omega}{z} \left\{ 1 + 2 \frac{e^{-\hbar\omega\beta}}{1 - e^{-\hbar\omega\beta}} \right\}$$

$$\overline{E} = \frac{N\hbar\omega}{Z} \left\{ 1 + 2e^{-\hbar\omega\beta} \right\}$$

$$= N\hbar\omega \left( \frac{1}{z} + e^{-\hbar\omega\beta} \right)$$

$$C = \frac{\partial E}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} E = -\frac{N + \omega}{k T^2} \left[ e^{-t + \omega \beta} \right] - t \omega$$

$$= N \frac{h^2 \omega^2}{k T^2} \left[ e^{-t + \omega \beta} \right]$$

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a) 
$$P_{S} = \frac{e^{-E_{S}B}}{Z} / \frac{e^{-E_{I}B}}{Z}$$

$$= e^{-E_{S}B} e^{E_{I}B} = e^{-(E_{S}-E_{I})}\beta = 0$$
This is only possible if  $(E_{S}-E_{I})\beta = \infty = 0$ 

$$= 0$$

$$= 0$$

$$= 0$$

$$= 0$$

$$= 0$$

$$= 0$$

This is only possible if T-DO

b) Reversing the above,  $T \rightarrow 0 \Rightarrow B \Rightarrow 0 \infty \Rightarrow 0 \in -(E_S - E_I)B \rightarrow 0$ So if  $T \rightarrow 0 = \frac{P_S}{P_I} \rightarrow 0$ .

c) In general 
$$S = +k \ln 2 + \frac{E}{7}$$
. Now  $E = E_1$ 

$$S = k \ln \left\{ \sum e^{-E_3 B} \right\} + \frac{E}{7}$$

$$= k \ln \left\{ e^{-E_1 B} \left( 1 + e^{-(E_2 - E_1)} \beta_{+} e^{-(E_3 - E_1)} \beta_{+} ... \right) \right\} + \frac{E}{7}$$

$$= k \left\{ \ln e^{-E_1 B} + \ln \left( 1 + ... \right) \right\} + \frac{E}{7}$$

$$= k \left\{ -E_1 B \right\} + k \ln \left( 1 + ... \right) + \frac{E}{7}$$

$$= -\frac{E_1}{7} + \frac{E_1}{7} + k \ln \left( 1 + ... \right) - D = 0.$$

$$= \sqrt{\frac{36}{57}} \sqrt{1} + \sqrt{\frac{36}{5P}} \sqrt{1}$$

$$= \left(\frac{36}{57}\right) \sqrt{1} + \left(\frac{36}{5P}\right) \sqrt{1}$$

and 
$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T} = P - \left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

Thus 
$$\left(\frac{\partial V}{\partial T}\right)_{P} = -\left(\frac{\partial S}{\partial P}\right)_{T}$$
 But if S-DO as T-DO

 $= \delta S = -\left(\frac{\partial F}{\partial T}\right) V N$ 

a) 
$$F = E - TS$$

$$dF = dE - TaS - SdT$$

$$= IdS - PdV - IdS - SdT + \mu dN = 0 dF = -PdV - SdT + \mu dN$$

$$S = Nk \frac{\partial}{\partial T} \left\{ T \left[ \ln V + \frac{3}{2} \ln \left( \frac{mkT}{2\pi h^2} \right) \right] \right\}$$

$$= Nk \left[ \ln V + \frac{3}{2} \ln \left( \frac{mkT}{2\pi h^2} \right) \right] + NkT \frac{3}{2} \frac{1}{T}$$

$$= \frac{3}{2} Nk + Nk \left\{ \ln V + \frac{3}{2} \ln \left( \frac{mkT}{2\pi h^2} \right) \right\}$$

b) 
$$\mu = + \left(\frac{\partial F}{\partial N}\right)_{T,V} \Rightarrow \mu = -kT \left[\ln V + \frac{3}{2}\ln\left(\frac{mkT}{2\pi\hbar^2}\right)\right]$$

c) The gas with molecules with smaller mass (A) has larger chemical potential (from part 5). So in order to reach equilibrium particles must leave this gas and enter the other. So flow from A to B.

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a) 
$$Z = \int e^{-E(x,p)\beta} dx dp$$
  

$$= \int e^{-p^{2}\beta/2m} e^{-U(x)\beta} dx dp$$

$$= \int e^{-p^{2}\beta/2m} dp \int e^{-U(x)\beta} dx$$

$$= Z_{p}$$

$$Z_{x}$$

b) 
$$p(x) = \frac{1}{Z} \int e^{-\frac{1}{2}(x,p)\beta} dp$$

$$= \frac{1}{Z} \int e^{-\frac{1}{2}p^2} \int e^{-\frac{1}{2}(x)\beta} dp$$

$$= \frac{e^{-\frac{1}{2}(x)\beta}}{Z} \int e^{-\frac{1}{2}p^2} \int e^{-\frac{1}{2}p^2} dp$$

$$= \frac{e^{-\frac{1}{2}(x)\beta}}{Z} \int e^{-\frac{1}{2}p^2} \int e^{-\frac{1}{2}p^2} dp$$

But 
$$Z=Z\times Zp$$
 gives  $P(x)=\frac{e^{-U(x)B}}{Zx}$ 

$$= \int_{X} p(x) dx$$

$$= \int_{Z_{x}} x e^{-u(x)\beta} dx$$

$$= \frac{1}{Z_{x}} \int_{X} x e^{-u(x)\beta} dx$$

d) Here 
$$u(x) = \frac{1}{2}m\omega^2 x^2$$
 and  $-\infty < x < \infty$  gives:

$$\overline{x} = \frac{1}{Z_X} \int x e^{-x^2 M \omega^2 \beta} dx$$

$$= 0.$$

e) If released from rest particle would go to y=0 since by is in regarive y direction.

$$\overline{y} = \frac{1}{z_y} \int y e^{-mgy} dy$$

$$\overline{y} = \frac{1}{z_y} \int y e^{-mgy\beta} dy$$
 with  $z_y = \int e^{-mgy\beta} dy = \frac{1}{mg\beta} = \frac{kT}{mg}$ 

So 
$$\overline{y} = \frac{mg}{kT} \int_{0}^{\infty} y e^{-mgy\beta} dy = \frac{mg}{kT} \left\{ \frac{y}{mg\beta} e^{-mgy\beta} dy \right\}$$

$$= \frac{1}{mg\beta} = p \left( \overline{y} = \frac{kT}{mg} \right)$$

Not be some \$0